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THE STABILITY OF ALKYL LEAD SALTS IN AIR, WATER, AND GASOLINE

PURPOSE

To determine to what extent alkyllead (RPbX) salts disproportionate on storage at room temperature in air, water, and gasoline to yield tetraethyllead.

SUMMARY

The stability on storage at room temperature in air, water, and gasoline of the following alkyllead salts: triethyllead chloride, triethyllead bromide, triethyllead carbonate, diethyllead dichloride, diethyllead dibromide, and diethyllead carbonate has been tested.

Of the above, only triethyllead carbonate (containing some triethyllead bicarbonate) showed appreciable decomposition with the formation of tetraethyllead in the three media; in gasoline and in water, in four and one-half months this mixture gave about 23 percent of tetraethyllead on the basis of the lead present in the original material; while in air, the amount of decomposition was 18 percent in the same time.

Diethyllead dibromide showed 12 percent decomposition in four and one-half months in gasoline, a result somewhat at variance with previous behavior in that steam distillation of this salt yields triethyllead bromide which in turn decomposes to tetraethyllead (see LED's 38-2 and 38-25). In the present tests, triethyllead bromide showed practically no decomposition in the three media tested.

All the other salts tested showed only negligible decomposition in either air, gasoline, or water.

INTRODUCTION

Previous work(1) done in this laboratory has shown that

(1) LED 38-2 Steam Distillation of Diethyllead Dibromide.
LED 38-25 Steam Distillation of Triethyllead Bromide.
LED 38-27 Steam Distillation of Diethyllead Dichloride.
LED 38-35 Steam Distillation of Triethyllead Chloride.
LED 38-57 Steam Decomposition of Triethyllead Hydroxide and Diethyllead Hydroxide.
LED 39-3 Preparation and Steam Decomposition of Triethyllead Carbonate and Diethyllead Carbonate.

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alkyllead salts decompose on steam distillation in accordance with the following equations:

$$2\ Et_3PbX \longrightarrow Et_4Pb + Et_2PbX_2 \qquad I$$
$$2\ Et_2PbX_2 \longrightarrow Et_3PbX + PbX_2 + EtX \qquad II$$
$$Et_2PbX_2 \longrightarrow PbX_2 + 2\ Et \qquad III$$

where X = Cl, Br, or CH. The net results in the case of the triethyllead halides is the sum of I plus II and of I plus III, and may be represented by the following equations:

$$3\ Et_3PbX \longrightarrow 2\ Et_4Pb + PbX_2 + EtX \qquad IV$$
$$2\ Et_3PbX \longrightarrow Et_4Pb + PbX_2 + 2\ Et \qquad V$$

During the steam distillation of triethyllead carbonate and diethyllead carbonate, these salts are first hydrolyzed to the corresponding hydroxides, triethyllead hydroxide and diethyllead hydroxide, respectively. Triethyllead hydroxide then decomposes mainly in accordance with I, while diethyllead hydroxide decomposes mainly in accordance with III. Under favorable conditions, the steam decomposition of some of these salts may yield theoretically as much as 67% tetraethyllead on the basis of the lead present in the original salt.

In view of the safety hazard involved in cleaning out sludges from Ethyl Fluid and leaded-gasoline storage tanks and tank cars, it seemed of importance to study the stability during storage in air, water and gasoline of these same salts which might be present in sludges, i.e., to determine to what extent they disproportionate to yield tetraethyllead. This report covers such a study.

EXPERIMENTAL

Materials

A. Alkyllead Salts. - Triethyllead chloride, triethyllead bromide, triethyllead carbonate, diethyllead dichloride, diethyllead dibromide and diethyllead carbonate were prepared and analyzed by methods previously described(1); the analyses were as follows:

	Analysis			
	Pb		X	
Alkyllead Salt	Calcd.	Found	Calcd.	Found
Et_3PbCl	62.8	62.9		
Et_3PbBr	55.4	55.5	21.4	21.2
$(Et_3Pb)_2CO_3$(a)	63.9	60.6		
Et_2PbCl_2	61.6	61.9	21.1	21.0
Et_2PbBr_2	48.8	49.0	37.6	37.2
Et_2PbCO_3	63.7	64.3		

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(a) This salt was prepared by treatment of triethyllead hydroxide with carbon dioxide, followed by vacuum dessication of the resulting triethyllead bicarbonate for two weeks, a procedure which ordinarily gives pure triethyllead carbonate. However, in this case the reaction was not complete and the analysis indicated an approximately equal molar mixture of triethyllead carbonate and triethyllead bicarbonate; titration with hydrochloric acid indicated the absence of diethyllead carbonate or hydroxide.

B. Gasoline. - An unleaded natural gasoline (prepared from refinery gases) was used in the tests involving the triethyllead chloride, triethyllead bromide and diethyllead dibromide salts. When it was discovered that this gasoline gave an emulsion with the ammonia water used to extract the alkyllead salts, its use was discontinued and White Red Crown was used in the triethyllead carbonate, diethyllead dichloride, and diethyllead carbonate tests, which were started over a month later.

PROCEDURE

A set of 12 test-tubes with cork stoppers bearing short lengths of capillary tubing was provided for the tests with each alkyllead salt. Approximately 2 g. of the salt were placed in each test-tube. To four of the test-tubes containing a particular salt were added 25 cc. of distilled water; to a second four were added 25 cc. of gasoline; while the remaining four were allowed to stand exposed to air. The stoppers bearing the capillary tubing were then put in place and the tubes were stored in a dark box at room temperature.

At storage-time intervals of one, two, and four and one-half months, test-tubes of the various salts in the different media were removed from the storage box, and the contents were extracted with hexane to remove the tetraethyllead formed. The hexane extracts were then shaken with 29% ammonia water to remove any alkyllead salts extracted by the hexane. This was followed by a water wash to remove most of the ammonia retained by the hexane. The lead remaining in the hexane as tetraethyllead was finally determined by analysis.

RESULTS

In Table I are given the amounts of decomposition, as measured by the amount of tetraethyllead formed, for the various salts in one, two and four and one-half month storage periods; the amount of decomposition for each salt is given in terms of percent of the lead input converted to tetraethyllead. Figure 1 shows graphically the rate of decomposition for each of the alkyllead salts in the various media.

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TABLE I - THE DECOMPOSITION OF RPbX SALTS AT ROOM TEMPERATURE

Salt	Series	Medium	Total percent TEL formed (a) 1 month	2 months	4½ months
Et_3PbCl	I	Air	0.02	0.00	0.00
		Water	.02	.00	.02
		Gasoline(b)	.08	.04	.16
Et_3PbBr	III	Air	0.06	0.17	0.03
		Water	.05	.02	.01
		Gasoline(b)	.30	.22	.40
$(Et_3Pb)_2CO_3$(d) $+Et_3PbHCO_3$	VI	Air	2.98	8.03	17.65
		Water	15.83	21.70	23.38
		Gasoline(c)	6.15	10.96	21.50
Et_2PbCl_2	IV	Air	0.00	0.03	0.00
		Water	.00	.02	.00
		Gasoline(c)	.22	1.34	.36
Et_2PbBr_2	II	Air	0.05	0.00	0.01
		Water	.03	.04	.04
		Gasoline(b)	9.07	9.08	12.25
Et_2PbCO_3	V	Air	0.01	0.02	0.00
		Water	.02	.01	.01
		Gasoline(c)	.03	.03	.02

(a) Based on the amount of lead present in the original salts; the analyses were made on the contents of separate test-tubes after they had stood the indicated length of time.
(b) Natural gasoline.
(c) White Red Crown.
(d) An approximately equimolar mixture of the two salts.

These results show that: (a) only the mixture of triethyllead carbonate and bicarbonate gave appreciable decomposition with the formation of tetraethyllead in air, water, and gasoline. The rate of decomposition of this mixture was faster in water than in either air or gasoline, and the maximum amount of decomposition (22 to 23 percent) was reached in a storage time of two months. In gasoline, the amount of the lead input converted to tetraethyllead in four and one-half months was 22%; while in air, the amount converted in the same time represented 18% of the lead input. From Figure 1, it should be noted for the triethyllead carbonate mixture in both gasoline and air, the amount of decomposition is almost a linear function of time.

(b) Diethyllead dibromide in gasoline gave 9% decomposition to tetraethyllead in one month and 12% decomposition in four and one-half months; in water and air, only negligible decomposition to tetraethyllead was noted in the time intervals studied. This behavior of diethyllead dibromide in gasoline is surprising in view of the fact that triethyllead bromide, the salt to which the dibromide

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decomposes in accordance with equation II, gave no decomposition to tetraethyllead in any media in the present tests. This suggests that the course of the decomposition of diethyllead dibromide in gasoline at room temperature under the present conditions is not the same as it is when it is decomposed with steam.

(c) The remaining salts tested gave only negligible decomposition in either air, water or gasoline.

CONCLUSIONS

On the basis of the results obtained in these tests, it appears that triethyllead carbonate or bicarbonate decomposes on storage at room temperature in air, water and gasoline to give tetraethyllead, while diethyllead dibromide decomposes only in gasoline. On the other hand, the triethyllead halides, diethyllead chloride and diethyllead carbonate appear to be remarkably stable under the same conditions.

Only a little is known concerning the formation[1] and presence[2] of triethyllead carbonate and bicarbonate in sludges from Ethyl Fluid and Ethyl Gasoline. In view of the fact that the present tests show that these salts may contribute greatly to the toxic hazards of sludges, it is suggested that further examinations be made regarding the formation and presence of these compounds in sludges obtained from Ethyl Fluid and Ethyl Gasoline.

(2) LTD 38-41 - Stability Tests on Lead Tetraethyl in Ethylidene Chloride and Propylene Chloride
LTD 39-49 - Formation and Analysis of Sludge from Ethyl Fluid

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